

# **A PREDICTIVE MODEL FOR DETERMINING INDOOR CONCENTRATIONS OF OUTDOOR VOLATILE ORGANIC COMPOUND AIR TOXICS**

## **Interim Project Report**

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### **ABSTRACT**

Effective regulation of hazardous air pollutants (HAPs) requires an understanding of exposure routes, especially indoors where Americans spend most of our time. Indoor exposures to HAPs generated outdoors are affected by an array of physical-chemical processes that occur at different rates indoors vs. outdoors. The goal of this research is to develop and demonstrate a modeling system to predict time-resolved residential concentrations of HAPs using outdoor air composition data as input. The model focuses on volatile organic compounds (VOC-HAPs) that are associated with activities and products of the oil and gas industries. Key processes are simulated by computational solution of differential equations that represent fundamentally or semi-empirically the underlying physical and chemical processes. The model simulates the entry and removal of gas-phase compounds via ventilation, photolytic and gas-phase chemistry of the indoor air mixture, depositional losses to indoor surfaces, and the reversible sorption of some compounds following deposition onto indoor surfaces. Emissions from indoor sources are also considered since they can affect the indoor chemistry of HAPs entering from outdoors. Indoor photolysis reactions are estimated to occur at a fraction of outdoor rates, calculated with an LBNL-developed actinic flux model. Chemistry is modeled using the SAPRC-99 chemical mechanism. Our progress to date includes construction and testing of an alpha version of the modeling system and extensive testing to verify the performance and validate the applicability of individual model components. We have also designed and initiated an experimental program to measure equilibrium partitioning and sorption kinetic parameter values for VOC-HAPs in a room-sized test chamber constructed and furnished with surfaces and materials that are typical of residential environments. The data generated from these experiments will be used to support the sorption component of our indoor air modeling system.

**BACKGROUND:**

The Clean Air Act Amendments of 1990 (CAA) established a new regulatory category for 188 hazardous air pollutants (HAPs), or "air toxics." These compounds are known or believed to be toxic to humans and are emitted in large quantities by industrial sources. One of EPA's goals is to reduce air toxic emissions by 75% of the 1993 levels. Subsequently, EPA plans to base the HAP standards on risk. The importance of both the inhalation pathway and the role that indoor concentrations of HAPs play in human exposure and risk assessment has recently been noted by a sub-committee of the EPA Science Advisory Board.

Activities and products of the oil and gas industry are thought to be major contributors to the total national emissions of several volatile organic compounds (VOCs) listed as HAPs (see Table 1). These VOC-HAPs are emitted as fugitive emissions from oil refining, products of combustion of fuels made by refineries, and as evaporative emissions from fuels produced for mobile sources.

In contrast to the six "criteria" air pollutants, for which health-based ambient (outdoor) concentration limits have been set, much less is known about typical concentrations, actual population exposures, and "safe" levels of HAPs. Recognizing this uncertainty, a sub-committee of EPA's Science Advisory Board has suggested that research be conducted so that risk can be assessed. Quantifying risk requires that exposure be known. Since Americans spend ~90% of their time indoors (~70% in residences), much of the exposure to air contaminants occurs through the medium of indoor air. The Science Advisory Board specifically recommended research to establish the relationship between outdoor HAP concentrations and those that result indoors from outdoor sources. Such research will improve modeling of personal and population exposures to HAPs from outdoor sources, and ultimately provide the scientific data needed to optimize controls.

**Table 1.** Volatile organic compounds identified as hazardous air pollutants (VOC-HAPs) that are associated with activities and products of the oil and gas industry.

Compound	Mobile source contribution to total national emissions <sup>1</sup>
1,3-Butadiene	60%
Acetaldehyde	70%
Acrolein	39%
Benzene	76%
Ethylbenzene	84%
Formaldehyde	49%
Hexane	44%
MTBE	86%
POM <sup>2</sup>	6%
Styrene	40%
Toluene	74%
Xylenes	79%

<sup>1</sup> Source: Control of Emissions of Hazardous Air Pollutants from Motor Vehicles and Motor Vehicle Fuels. U.S. EPA Office of Transportation and Air Quality, Report # EPA-420-R-00-023 December 2000. Estimates from the 1996 National Toxics Inventory. These illustrate the relevance of these compounds to the oil and gas industry.

<sup>2</sup> Polycyclic organic matter; calculated as the sum of 7 polycyclic aromatic hydrocarbons.

**OBJECTIVE:**

In response to the need to quantify human exposure to HAPs so that risk may be assessed, we are conducting research whose objective is to develop a physically based semi-empirical model to predict time-dependent indoor concentrations of air toxics of outdoor origin. The research will provide tools for assessing exposure. The HAPs of interest are volatile organic compounds (VOCs) that derive from activities and products of the oil and gas industry.

**APPROACH:**

We are constructing a mass balance model to track the transport and fate of VOCs that enter a residential interior space with ventilation and infiltration air. The model accounts for key physical and chemical transport and transformation mechanisms that can affect indoor pollutant concentrations of outdoor origin. Exercising the model will facilitate both predictive and diagnostic examinations of indoor exposure to outdoor VOCs. The model is designed to simulate residential conditions, and it is applicable to other environments. Residences are modeled as spaces with uniform emissions, concentrations, and surface to volume ratios throughout, i.e. as continuous flow stirred tank reactors (CFSTR, a chemical engineering construct). The model can be used to estimate the concentration of outdoor HAPs in the indoor environment using outdoor pollutant monitoring data, meteorological data, and available data for the housing stock. We define the model as “semi-empirical” since the mathematical forms of the governing equations are consistent with the dominant physical and chemical processes, and they rely on parameters that are determined from experiment. The model can be represented mathematically as a collection of differential equations describing the time-dependent indoor concentrations  $C_i$  of gas-phase compounds  $i$ , as show below in Equation 1:

$$\frac{dC_i}{dt} = p\lambda C_{i,amb} - \lambda C_i + \frac{E_i}{V} - \sum_{j=1}^n R_{ij} + \sum_{j=1, k=1}^n R_{jk} - \sum_{l=1}^n k_{a,il} C_i S_l + \sum_{l=1}^n k_{d,il} M_{il} S_l \quad (1)$$

Terms:      (1)      (2)      (3)      (4)      (5)      (6)      (7)

Each term of this equation represents a physical-chemical process that can affect the concentration of compound  $i$ . In some cases, compounds having similar physical-chemical behavior are grouped (lumped) to achieve computational efficiencies. Lumping also is employed because there are insufficient fundamental data to justify the treatment of some compounds on an individual basis. The **first term** of Eq. (1) describes the entrance of the compound via ventilation:  $C_{i,amb}(t)$  [ $\mu\text{g m}^{-3}$ ] is the time-dependent concentration of compound  $i$  in ambient (outdoor) air;  $\lambda$  [ $\text{min}^{-1}$ ] is the air change rate; and  $p$  [unitless] is the penetration efficiency (theoretically ranging from 0 to 1 that is set initially to 1 for all compounds). The **second term** accounts for the removal of mass via ventilation. The **third term** accounts for indoor emission sources, with  $E_i(t)$  representing the time-dependent residential emission rate [ $\mu\text{g min}^{-1}$ ]. While this research focuses on tracking HAPs generated outdoors, indoor emissions must also be considered since the chemistry is very non-linear and the indoor emissions can affect the indoor chemistry of HAPS of outdoor origin. Homogeneous (i.e. gas-phase) chemical reactions are represented in the **fourth and fifth terms**.  $R_{ij}$  is the reaction rate for compound  $i$  reacting indoors with another compound via a reaction that consumes both  $i$  and  $j$ .  $R_{jk}$  is the rate of reaction for two compounds  $j$  and  $k$  that react to form  $i$ . This formulation represents bimolecular reactions, but

both consumption and formation reactions can have other forms. For example, there can be limited photolytic activity indoors, and in such cases, a single compound is activated by light of a specific wavelength, and forms other species. This will be discussed subsequently. The *sixth term* accounts for deposition of the gas-phase compound  $i$  to an indoor surface  $l$ ; where  $k_{a,il}$  is the deposition velocity [ $\text{m min}^{-1}$ ] of compound  $i$  on surface  $l$  and  $S_l$  [ $\text{m}^2 \text{m}^{-3}$ ] is the projected-surface area to room volume ratio associated with material  $l$ . For some compounds, such as ozone, deposition is followed by a surface reaction or other chemical interaction that represents an irreversible loss mechanism. Alternatively, deposition can lead to a reversible, physical binding (i.e. sorption). In these cases, the mass of compound sorbed on the surface is tracked explicitly as  $M_{il}$  [ $\mu\text{g m}^{-2}$ ] and desorption is modeled in the *seventh term* with  $k_{d,il}$  [ $\text{min}^{-1}$ ] representing the desorption rate of compound  $i$  from surface material  $l$ . The model can treat “n” indoor surface materials; however in its current form the indoor environment is represented as a single material with a surface to volume ratio of 2 [ $\text{m}^2 \text{m}^{-3}$ ]. The treatment of material surfaces will be refined as appropriate data become available. For some of the processes described above, e.g. chemical reactions, the model is a fundamental representation of the physical process. For others, e.g. sorption, the mathematical formulation is a semi-empirical description of observed phenomena.

Note: for clarity of mass balance, the equations above have been described for species concentrations in units of mass per volume. As formulated, the model explicitly tracks concentrations in ppm, or part-per-million units. The two formulations are operationally equivalent and interchangeable through a straightforward conversion factor.

## PROGRESS ON MODEL DEVELOPMENT AND EVALUATION:

We have constructed an alpha version of our mass balance model that parameterizes the key physical and chemical processes described above. The initial modeling system represents the synthesis of existing component models (e.g. for sorption and chemistry) and contains parameter values obtained primarily from the scientific literature. In parallel to verifying and evaluating the code and basic components of the model, we are reviewing the pertinent scientific literature associated with the fate and transport of compounds in the indoor environment to obtain values of key parameters necessary for the model. We are also conducting our own experiments to measure sorption kinetic rates and equilibrium partitioning for VOC-HAPs of interest. The experiments are described in the last section of the report. The text below describes the chemical mechanism and initial values of parameters that are used in the alpha version of the model.

Verification of a model is the process of determining if a computational simulation accurately represents the conceptual model, but no claim is made of the relationship between the simulation and the real world. The fundamental strategy of verification is to identify and quantify errors in the computational solution. Verification has to do with examining the code and numerics that are brought to bear to exercise the model. In contrast, validation is defined as the process of determining the degree to which a model is an accurate representation of the real physical world from the perspective of the intended uses of the model. Verification and validation are ongoing efforts that do not have a clearly defined end point since model complexity tends to grow with an increased understanding of a subject. In complex codes, like the one being developed here, errors are inevitable during the development stage. Considerable effort must be directed toward verification to eliminate and correct any coding or numerical errors. The text below describes a number of computer experiments that were conducted to verify that our code is functioning properly and to validate that our model is a faithful

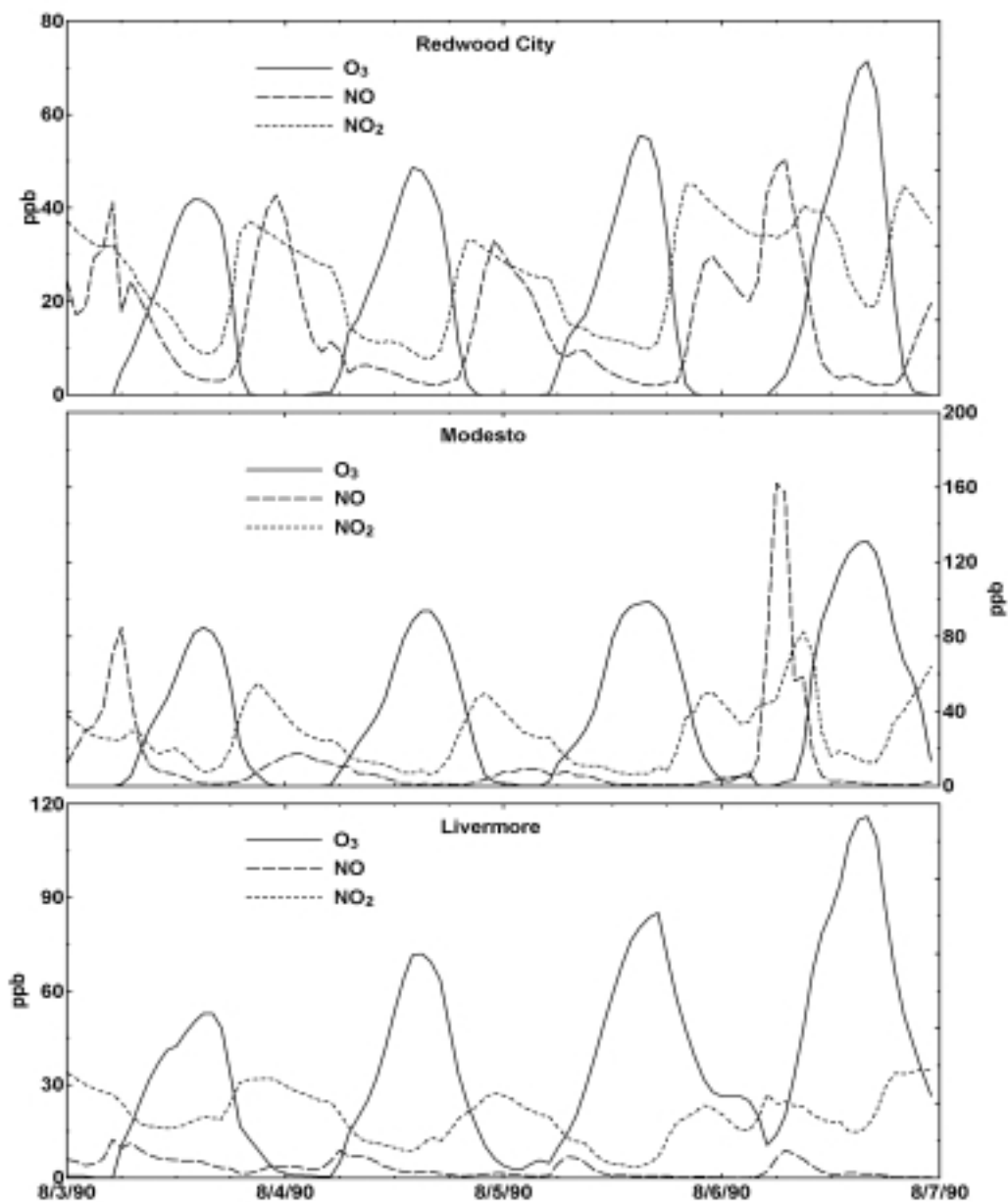
representation of the fate and transport of outdoor VOCs in the indoor environment. Our approach was to test code components by isolating one physical-chemical process at a time and run the model under conditions for which the expected model output is known or can be inferred from external sources, fundamental theory, or the accumulated past experience of the research team.

**The Chemical Mechanism.** Our modeling system represents chemistry using an expanded version of the SAPRC-99 mechanism developed and maintained by the California State Air Pollution Research Center (Carter, 2000). SAPRC-99 is the most complete representation of gas-phase atmospheric chemistry; it includes up-to-date mechanistic information and rate coefficients, is publicly available, and is widely used. The mechanism was designed for outdoor urban and regional scale photochemical modeling, but the chemical rate equations and rate coefficients are fundamental and thus apply indoors. SAPRC-99 can be used in a simplified form with most VOCs grouped into a few lumped species or expanded with reactions and rate data to track individual species of interest. For example, isoprene can be followed independently or lumped with other alkene compounds having related structures and participating in similar reactions. We customized the mechanism to focus on specific individual VOC-HAPs of interest to the oil and gas industry. This formulation explicitly treats most of the VOC-HAPs listed in Table 1 and is suitable for use with the dataset of outdoor concentrations described below. The full list of SAPRC-99 species included in our alpha model is provided as Table A-1.

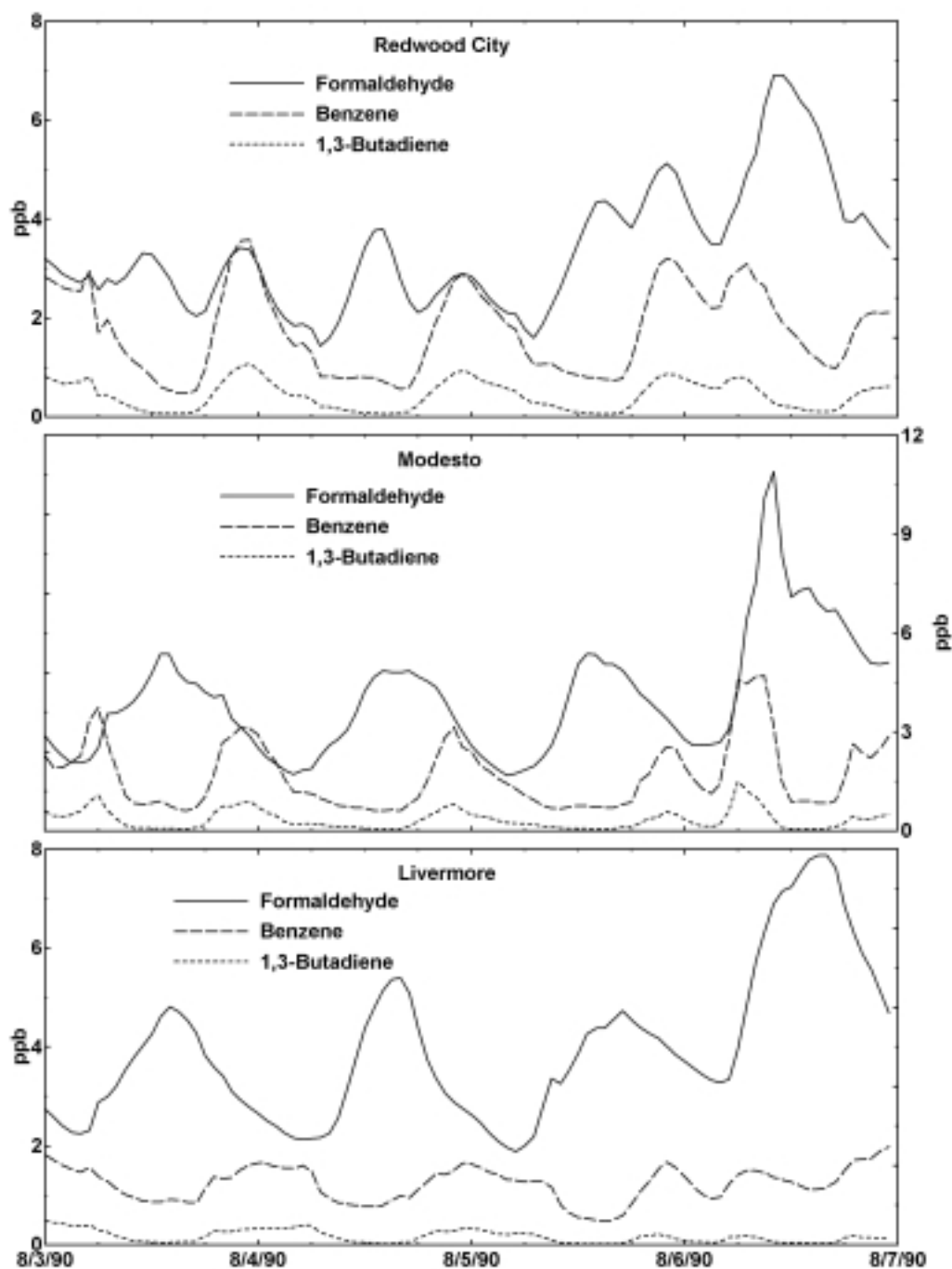
**Outdoor Air Composition.** The modeling system is designed to predict time-resolved indoor concentrations based on time-resolved outdoor concentrations of the species shown in Table A-1. Outdoor concentrations can be measured, modeled or set to hypothetical or design values. Concentrations of some species, including ozone and nitrogen oxides ( $\text{NO}_2$  and  $\text{NO}$ ) are measured hourly at EPA-designated monitoring stations throughout the U.S.; time-resolved data for these species are thus available for many locations. In contrast, concentrations of many VOC are routinely measured only on a 24-h time averaged basis, only at select stations, and on a restricted schedule because of the high cost of speciated VOC analysis. Only very sparse ambient data are available for aldehydes and highly reactive species. There are even fewer measurements of radical species concentrations, and they are often estimated by modeling. As a result, outdoor data appropriate for application of the indoor model generally can be developed in two ways: (1) through use of a photochemical modeling system to predict all relevant species concentrations in a given area; or (2) by combining time-resolved measurements with “typical” or reasonable values for species not measured in a particular instance. We have chosen to use outdoor model output because it provides the most complete description available of the outdoor air mixture over a diurnal cycle for several days in several locations. These modeled outdoor species concentrations have been used to test specific components of our indoor model and will be used as base-case scenarios for model application.

We have obtained outdoor data consisting of hourly gas-phase species concentrations predicted for three Northern California sites during a four-day ozone episode in August 1990 (Marr, 2002). These results are in the form of SAPRC-99 species concentrations, obtained from carefully constructed and validated 3-D photochemical modeling of the entire Northern California region, including the Bay Area, Sacramento, and Central Valley. Specifically, we are using data from one coastal and two inland grid cells that include Bay Area Air Quality Modeling District (BAAQMD) monitoring sites in Redwood City, Livermore, and Modesto, CA.

Predicted time-dependent concentrations of several key air pollutants are shown for each site in Figures 1-2. The predicted concentrations of Marr agreed reasonably well with measured hydrocarbon species concentration values at 14 stations in the modeling domain, confirming that these are reasonable values for use in our modeling.



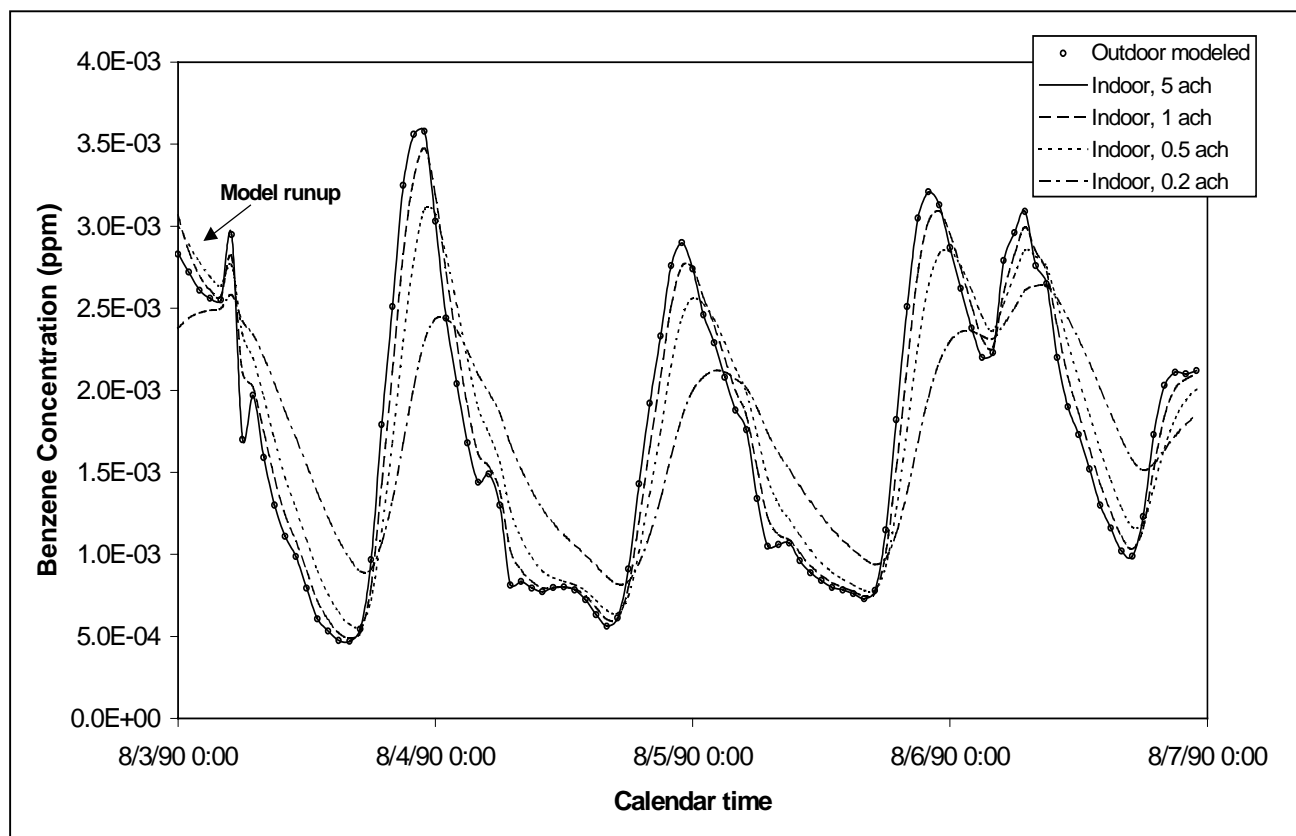
**Figure 1.** Photochemical model predicted outdoor concentrations of ozone and nitrogen oxides at three Northern California sites during a four-day ozone episode in 1990, as described in Marr (2002). The fully time- and chemically-resolved outdoor concentrations at these sites are being used as input data for our indoor model. Note that scales are not identical for the three locations, which experienced differing peak levels of ozone during this episode.



**Figure 2.** Photochemical model predicted outdoor concentrations of formaldehyde, benzene, and 1,3-butadiene at three Northern California sites during a four-day ozone episode in 1990, as described in Marr (2002). The fully time- and chemically-resolved outdoor concentrations at these sites are being used as input data for our indoor model.



**Verifying and Validating the Ventilation Component of the Model.** To determine whether the ventilation component of the model was behaving reasonably, we “turned off” all chemical reactions and set deposition and indoor emission rates equal to zero. As the ventilation rate increases, the time lag between outdoor and indoor concentrations should approach zero. The model was run over a range of ventilation rates, yielding results shown in Figure 3. As expected from stirred tank reactor theory, indoor concentration profiles mirror outdoor profiles at ventilation rates greater than 1.0 air changes per hour ( $\text{h}^{-1}$ ), but the indoor concentration profiles are smoothed and offset relative to the outdoor profile at ventilation rates below about  $0.5 \text{ h}^{-1}$ . The time offset is approximately the inverse of the ventilation rate. These results stress the importance of selecting appropriate time scales for comparing indoor vs. outdoor concentrations, i.e. over time scales much longer than ventilation.



**Figure 3.** Indoor and outdoor concentrations of benzene at varied ventilation rates with no indoor chemistry. These results demonstrate that at low ventilation rates, indoor concentration profiles are lagged in time compared to outdoor temporal profiles.

**Verifying and Validating the Deposition Component of the Model Code.** We evaluated the deposition mechanism in the code by setting outdoor concentrations to constant values over time, with chemistry still turned off. The alpha model incorporates deposition rates from Nazaroff and Cass (Nazaroff and Case, 1986), shown in Table A-2. The most critical of these rates is for ozone because ozone drives the indoor chemistry. The selected value of  $0.04 \text{ cm sec}^{-1}$  is consistent with results of a recent field study in which ozone deposition was measured in 43 Southern California

residences (Lee et al., 1999). A literature review of more recently measured deposition rates for ozone and other species is underway. CFSTR theory suggests that under the conditions described, indoor concentrations should reach steady-state levels that indicate a balance between introduction and losses by ventilation and losses with deposition. Model-output steady-state concentrations were exactly the same as those predicted from a mass balance calculation based on the ventilation rate, deposition rates, and surface to volume ratio used in the model runs. These results indicate that the deposition component of the model code is working properly.

**Determining the Importance of Indoor Photolysis Reactions.** Photolysis reactions arise from wavelength specific interactions between solar radiation and individual chemical compounds. They are important drivers of gas-phase chemistry outdoors but their relevance indoors has not been addressed in the literature. In the context of air quality modeling, photolysis reactions are parameterized with a rate coefficient  $J_x$  for a chemical species  $x$  that undergoes photolysis. The overall photolysis reaction rate is calculated by multiplying  $J_x$  with the species concentration  $C_x$ . The photolysis rate coefficient  $J_x$  is evaluated by integrating over wavelengths using the relationship

$$J_x = \int_0^{\infty} \sigma_x(\lambda) \phi_x(\lambda) F(\lambda) d\lambda \quad (1.1)$$

where  $\sigma_x(\lambda)$  is the absorption cross-section ( $\text{cm}^2$ ),  $\phi_x(\lambda)$  is the quantum yield, and  $F(\lambda)$  is the actinic flux ( $\text{photons cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$ ). For a specific molecule reacting in the troposphere, the lower limit of integration is frequently set at  $\lambda = 290 \text{ nm}$  and the higher limit is the longest wavelength where the photochemical reaction occurs (the reaction threshold). Most photolysis reactions of interest for air quality occur in the wavelength region  $\lambda = 290$  to  $420 \text{ nm}$  (*i.e.*, the near UV). The absorption cross-section and quantum yield for various reactions are measured in the laboratory. The actinic flux is calculated with a radiation transfer model. We use the LBNL (Vuilleumier et al., 2000) adaptation of the Tropospheric Ultraviolet-Visible (TUV) model by Dr. Sasha Madronich of the National Center for Atmospheric Research. This model has been shown by Vuilleumier et al. (Vuilleumier et al., 2001) to give very good agreement with experiments directed toward measuring the  $\text{NO}_2$  photolysis rate coefficient in the ambient atmosphere using an actinometer.

Actinic flux is converted to irradiance by integrating over wavelengths. Irradiance, or light intensity per area per time, varies outdoors by season, time of day, latitude, atmospheric composition (e.g., pollutant loading), and cloud cover – all of which affect the attenuation of sunlight passing through the atmosphere. The LBNL model accounts for these factors. Irradiance levels indoors are attenuated relative to outdoors. The clear glass installed in the vast majority of residences filters most light below about  $300 \text{ nm}$  but transmits light at higher wavelengths (through the visible) in roughly constant proportions (Rubin, 2002). Attenuation therefore should be roughly constant across wavelengths of interest to photochemistry and indoor photolytic reaction rates can be parameterized as a fixed fraction of outdoor values. This fraction will depend on overall light intensity indoors relative to outdoors, which will vary from room to room in a residence according to window area, directional exposure, outdoor shading (e.g. trees) and indoor window coverings (e.g. curtains and shades). To our knowledge, there has been no

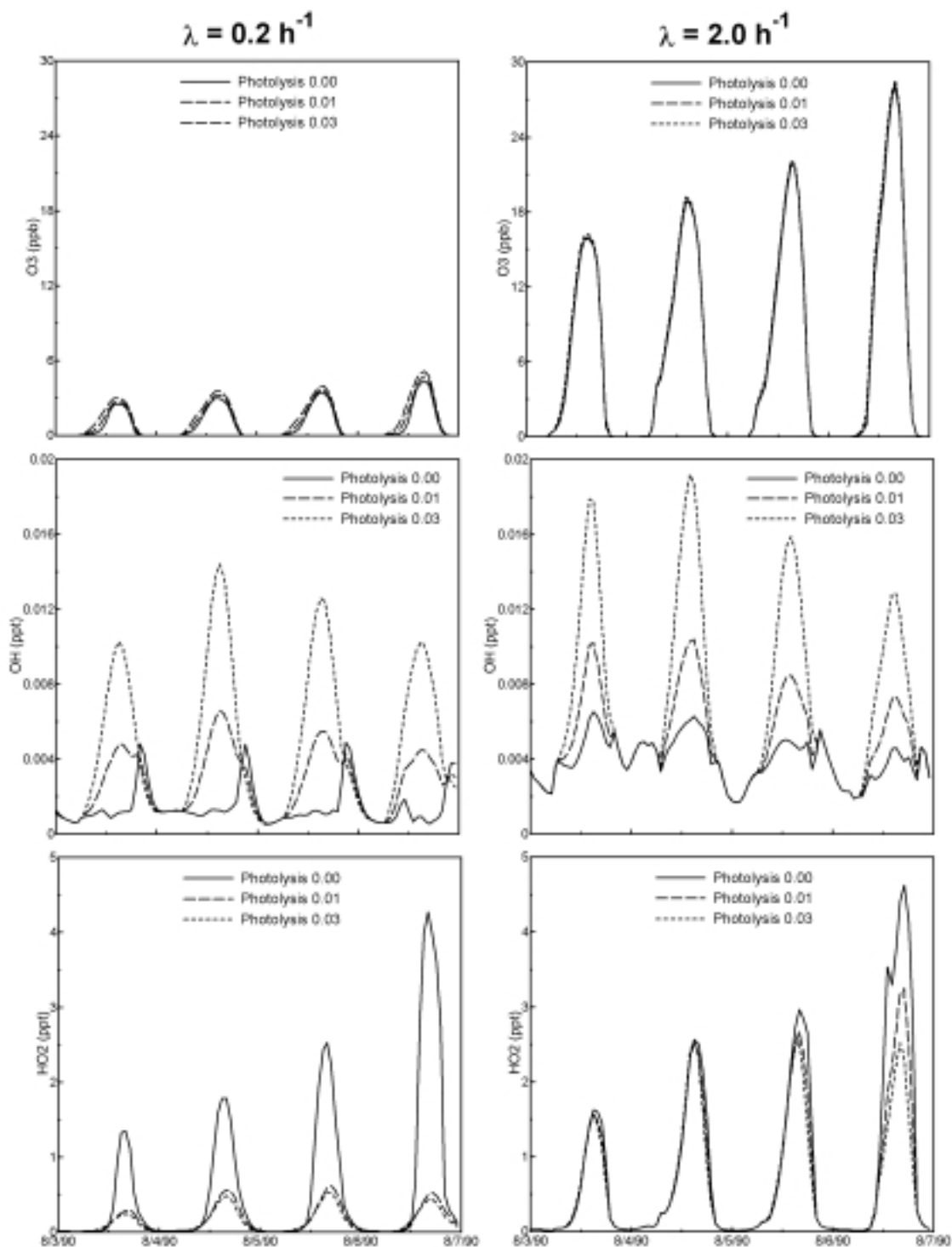
comprehensive effort, through measurements or modeling, to estimate the integrated wavelength-specific light intensity in a typical residential environment.<sup>1</sup>

In an attempt to gain some insight and to estimate an upper-bound for light intensity indoors, we conducted some range-finding measurements of irradiance in an old construction (ca 1910) home in Oakland, CA during the early afternoon of a summer day with clear skies. Irradiance levels were measured outdoors at the beginning and end of the experiments, and in the middle of each room of the house using a portable radiometer (Lightspex model RAD-rev A, McMahan Research Laboratories). Spectral distributions appeared similar indoors and outdoors; attenuation was thus evaluated by recording intensities (units of  $\mu\text{W}/\text{cm}^2/\text{nm}$ ) at 400 and 500 nm. Indoor light intensities of approximately 1-3% of outdoor midday values were measured in south or west facing rooms having windows along their entire length (shades completely open). Windowed, and naturally illuminated rooms facing north or east had light intensities of approximately 0.2-0.4% of outdoor values with shades open. Based on these measurements, we are currently using 3% of the outdoor actinic flux calculated with the LBNL model as an upper bound for indoor photolysis. These initial data also suggest that the integrated photolysis rate throughout an entire house is likely to be in the range of 0.1-1% of the corresponding outdoor value. Additional measurements are planned for the future.

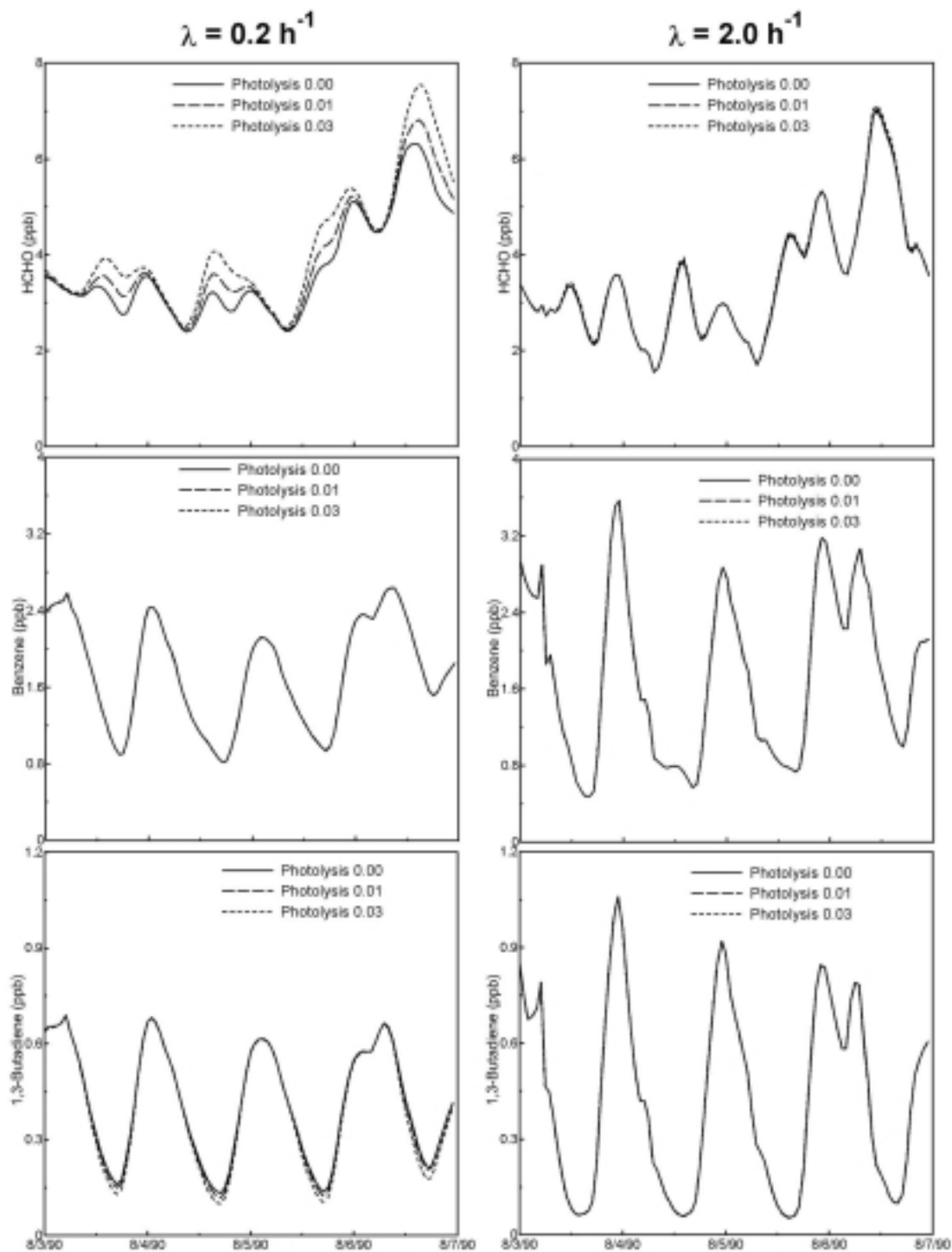
We evaluated the effect of setting indoor photolysis rates at 3%, 1%, and 0% of outdoor values by running the indoor chemistry model with time-resolved outdoor concentrations and deposition rates as described above, and ventilation set to 0.2, 0.6, and 2.0 air changes per hour. Selected results are shown in Figures 4-5. Changes in photolysis and ventilation rate each had a large effect on indoor OH and HO<sub>2</sub> radical concentrations, but ozone concentrations were affected only at the lowest ventilation rate (Figure 4), which corresponds to the longest residence time for chemistry to occur. Somewhat more puzzling is the fact that small or negligible effects were seen in the mean concentrations of most VOCs including some reactive compounds such as formaldehyde (Figure 5). This may result because the radical concentrations, while differing among scenarios, were still very low compared to typical midday outdoor values of 0.2 parts per trillion (ppt) (Weschler and Shields, 1996), resulting in overall low rates of chemical reactions that oxidize the VOCs. These results are still preliminary and have yet to be fully analyzed.

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<sup>1</sup> Nazaroff and Cass (1998) reported a measured attenuation factor of 99% (indoor light intensity 1% of outdoor values) for a Los Angeles area museum with a large skylight.



**Figure 4.** Model-predicted indoor concentrations of ozone and key radical species with indoor photolysis rates set to 0, 1%, and 3% of outdoor values at Redwood City, CA. Model run at ventilation rates of 0.2 and 2.0 air changes per h. Results indicate that indoor photolysis can have a large effect on indoor radical concentrations but effects on ozone are seen only at low ventilation rates.



**Figure 5.** Model-predicted indoor concentrations of formaldehyde, 1,3-butadiene, and benzene with indoor photolysis rates set to 0, 1%, and 3% of outdoor values at Redwood City, CA. See text for other model details. Model run at ventilation rates of 0.2 and 2.0 air changes per h. Results indicate that photolysis-induced changes in indoor radical concentrations (Figure 4) do not cause large differences in concentrations of VOC-HAPs, including reactive species.

**Comparison with University of Texas Calculations.** We were able to perform a validation computer experiment by setting up our model to approximate an indoor chemical modeling study by researchers at the University of Texas at Austin (Sarwar et al., 2002). Sarwar et al. focused on the study of OH and other radical concentrations produced from reactions of ozone with terpenes emitted from indoor sources. The general similarity of the two model formulations allowed comparison. We prepared an input file for our model that included the same indoor source emission rates used in the Sarwar et al. study. Outdoor concentrations were fixed at the levels of 16:00 on day 1 of our episode at the Redwood City site. These outdoor concentrations were selected because ozone was at 100 ppb, the value used in the Sarwar et al. study. We conducted a series of model runs employing various initial values of the ventilation rate, photolysis fractions (indoors vs. outdoors) and multiples of indoor alkene emission rates to mimic the range of conditions considered by Sarwar et al. Although our outdoor compositions were somewhat different and were actually more completely representative of urban atmospheric composition, the agreement was very satisfactory. Specifically, indoor OH radical concentrations obtained with our model showed the same dependence to the factors studied as reported in Sarwar et al.

**Sorption and Surfaces.** Our model currently defines only a single surface material for deposition and reversible sorption, but can be easily modified to include additional surfaces as sorption kinetic and equilibrium data become available. We have conducted a literature review of prior sorption studies and conceptual models. As noted earlier, the alpha model represents all sorption as fully reversible and thus includes only one sorption “compartment”. An additional irreversible sorption compartment can be added if warranted by the experimental results.

#### **PROGRESS ON EXPERIMENTAL INVESTIGATION OF SORPTION RATES:**

This section of the report describes progress in our experimental program to screen HAP-VOCs to identify those that sorb significantly enough to be included in our model and that require measurement of actual sorption rates.

The goal of our experimental program is to measure sorption kinetic rates and equilibrium partitioning values to support modeling of HAP sorption. This is important since sorption is a potentially important loss mechanism for some VOC-HAPs and therefore must be evaluated to estimate exposure, which is a critical component for evaluating risk. We determined that new experiments are needed to characterize sorption kinetics and equilibrium partitioning after conducting a comprehensive literature review. Sorption rates for individual VOCs on specific surface materials have been derived primarily from small-scale laboratory experiments and reported for several different mathematical representations of the sorption process (Borazzo et al., 1990; Colombo et al., 1993; Jorgensen and Bjorseth, 1999; Jorgensen et al., 1999; Piade et al., 1999; Tichenor et al., 1991; Van Der Wal et al., 1998; Van Loy et al., 1997; Van Loy et al., 2001; Won et al., 2000; Won et al., 2001). Our experiments are designed to address the two primary deficiencies found in the existing data by targeting many of the specific VOC-HAPs that are the focus of this project, and by measuring sorption rates in a realistic setting with multiple surface materials present in realistic proportions. Past studies have examined interactions between some VOC-HAPs shown in Table 1 (e.g. Toluene, Ethylbenzene, MTBE) with an array of common interior materials. Theoretically, the individual compound-material interactions can be added in parallel to our model to represent the many and varied surfaces and materials present in occupied residences. However, published efforts to validate the use of individual material

rates for the purpose of predicting VOC behavior in a full-scale residence have indicated potential problems with this extrapolation procedure (Tichenor et al., 1991; Won et al., 2001). For example, Won et al. (Won et al., 2001) found that toluene sorption was 9 times greater than values predicted by cumulative modeling of all surfaces in a Canadian research house. The literature data are also lacking since no parameter estimates are available for many of the compounds listed in Table 1. Some studies have demonstrated that sorption parameter values correlate to vapor pressure on a log-log scale, e.g. (Won et al., 2001). This facilitates order-of-magnitude predictions of sorption rates and equilibrium relationships for compounds that fall within the vapor pressure range for which the correlations were measured. Some of the VOC-HAPs of interest have vapor pressures that are outside the range presented in the Won study; hence, it is not clear that they can be predicted reliably from the relationships presented. The compounds we have selected to evaluate (shown in Table 2) will allow us to extend the range and to develop whole-room, multiple surface material rates for use with our indoor pollutant dynamics model.

Table 2. Compounds studied in preliminary sorption experiments.

Compound (*HAP)	CAS <sup>1</sup>	Formula	M.W. <sup>2</sup> (g/mol)	Class	V.P. <sup>3</sup> (Pa)	B.P. <sup>4</sup> (°C)
Acetaldehyde*	75-07-0	C2-H4-O	44.1	ALDEHYDE	1.2E+05	21
Isoprene*	78-79-5	C5-H8	68.1	ALKENE	7.3E+04	34
Acrolein*	107-02-8	C3-H4-O	56.1	ALKENE/ALDEHYDE	3.7E+04	53
2-Butanone* (MEK)	78-93-3	C4-H8-O	72.1	KETONE	1.2E+04	80
Benzene*	71-43-2	C6-H6	78.1	AROMATIC	1.3E+04	80
Toluene*	108-88-3	C7-H8	92.1	AROMATIC	3.8E+03	111
Ethylbenzene*	100-41-4	C8-H10	106.2	AROMATIC	1.3E+03	136
o-Xylene*	95-47-6	C8-H10	106.2	AROMATIC	8.8E+02	144
1,2,4 Trimethyl- benzene	95-63-6	C9-H12	120.2	AROMATIC	2.8E+02	169
1,3-Diethyl- benzene	141-93-5	C10-H14	134.2	AROMATIC	1.6E+02	182
Phenol*	108-95-2	C6-H6-O	94.1	AROM-ALCOHOL	4.7E+01	182
o-Cresol*	95-48-7	C7-H8-O	108.1	AROM-ALCOHOL	4.0E+01	191
Naphthalene <sup>5</sup>	91-20-3	C10-H8	128.2	BICYCLIC AROMATIC	1.2E+01	218
1-Methyl- naphthalene <sup>5</sup>	90-12-0	C11-H10	142.2	BICYCLIC AROMATIC	7.2E+00	245
2,3-Dimethyl- naphthalene <sup>5</sup>	581-40-8	C12-H12	156.2	BICYCLIC AROMATIC	1.9E+00	264

<sup>1</sup>CAS = Chemical Abstracts Service reference number

<sup>2</sup>M.W. = molecular weight (mass)

<sup>3</sup>V.P. = vapor pressure

<sup>4</sup>B.P. = boiling point

<sup>5</sup>Progression of sorption rates for homologous series of bicyclic aromatics used to infer sorption rates for higher molecular weight cyclic aromatics, including polycyclic aromatic hydrocarbons.

Experiments are being conducted in a full-scale, furnished space that is intended to approximate real indoor environments that contain multiple material surfaces. Measured sorption rates and equilibrium partitioning values for such spaces are crucial for our modeling efforts and will allow for validation of individual material values reported in the literature. The experiments

are designed to isolate net adsorption and net desorption phases by first measuring the decay of gas-phase concentrations following a spiked addition of a VOC mixture into the furnished chamber operating in static, or unventilated mode (adsorption) and then monitoring the growth of VOC concentration after the air in the chamber has been fully replaced and the chamber has been resealed (desorption phase). The experimental room is approximately the size of small living room or typical bedroom, with a volume of  $49.5\text{-m}^3$ . Current interior materials include  $64.2\text{ m}^2$  painted gypsum wallboard on all walls and ceiling,  $20.4\text{ m}^2$  carpet on the floor (without padding), four upholstered nylon fabric chairs ( $13.9\text{ m}^2$  projected surface area), two swaths of heavy cotton draperies ( $10.5\text{ m}^2$  projected surface area), and several wood veneer pieces with a total surface area of  $18.7\text{ m}^2$ .

To date, we have conducted experiments to test our methodology and determine approximate time scales of sorption for various compounds. Knowledge of the time scales is critical for the design of sampling schedules appropriate for quantifying adsorption and desorption rates in follow up experiments.

Prior to each experiment, the chamber was flushed with VOC-free air to remove previously sorbed compounds. Ventilation was then turned off and air samples were collected to measure background levels of target VOC-HAPs in the chamber following an equilibration period. Pure compounds were then introduced into the chamber by injecting liquid mixtures into one or two glass dishes placed directly in front of a small axial fan. The compounds tested in one or more experiments are shown in Table 2. Semi-volatile organic compounds (SVOC) were injected into a heated dish ( $\sim 80\text{ C}$ ) to promote quick volatilization. The air exchange rate of the sealed chamber was confirmed to be very low ( $<0.01$  air changes per h) by tracking the decay of  $\text{SF}_6$  injected at the same time or shortly after the VOCs. VOC concentrations were measured by collecting air samples on solid sorbent tubes containing Tenax-TA only or Tenax backed up by a second sorbent material to collect more volatile compounds. The dual sorbent technique allows for the collection of VOCs spanning a range from very volatile to semi-volatile. Samples were thermally desorbed and analyzed by GC/MS. Samples were collected from the sealed chamber at varying intervals over 1-2 days. At the end of this adsorption period, the chamber was quickly flushed and replaced with filtered fresh air to reduce the concentration of VOC-HAPs in chamber air. The chamber was then resealed and VOC samples were collected for another day or more.

Selected preliminary results from the pilot experiments are provided in Figure 6-8. Figure 6 includes data from two separate experiments, to illustrate the relative decay of lightly vs. heavily sorbing compounds. In experiment 1, gas-phase concentrations of the more volatile compounds decayed over several to tens of hours, equilibrating at levels of about half the initial gas-phase concentrations (meaning that about half of the mass was sorbed). These preliminary results indicate that even highly volatile compounds such as acrolein may sorb at rates relevant to indoor spaces with very low ventilation, e.g. in the range of 0.2-0.3 per h. By contrast, the much less volatile compounds from experiment 3 transitioned almost entirely from the gas-phase to the sorbed phase within a period of 1-2 hours; well over 90% of the emitted mass was sorbed by this time. Sorption thus appears to be an important process for SVOC at most real-world ventilation rates. These results indicate the need to use two distinct sampling schedules to quantify rates of all VOC-HAPs of interest.

Figure 7 shows how the measurements from the initial decay period can be used to estimate the adsorption rate. If desorption is assumed to be small, the natural logarithm of the concentration should decay linearly with a slope equal to the ventilation rate plus the adsorption rate (both in units of 1/h). With the very low air exchange rates in our experiment, the slope is a

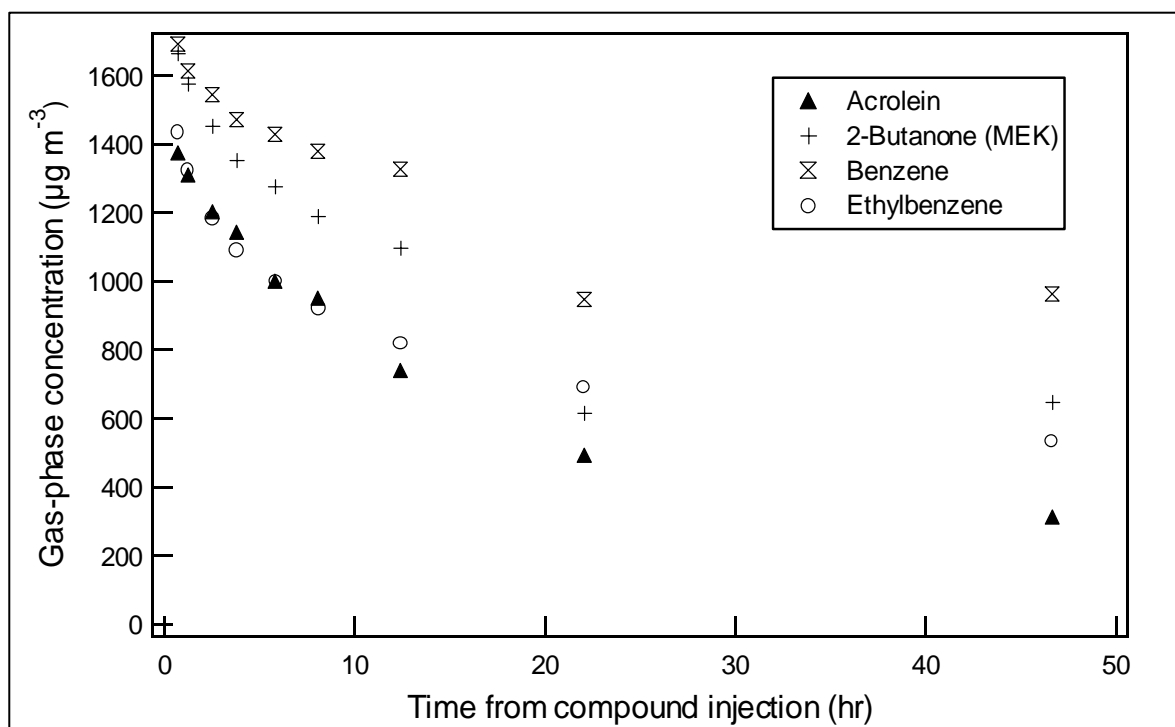


direct approximation of the adsorption rate. The relationship works very well for the volatile compounds, but the apparent curvature for the less volatile compounds in (b) indicates that even within one hour desorption must be considered when attempting to determine rates by curve fitting. These data are being re-analyzed and fit to a model that includes both adsorption and desorption, yielding somewhat higher adsorption rates. It is also important to note that the direct estimate is still very useful as a check on the curve fitting with desorption included.

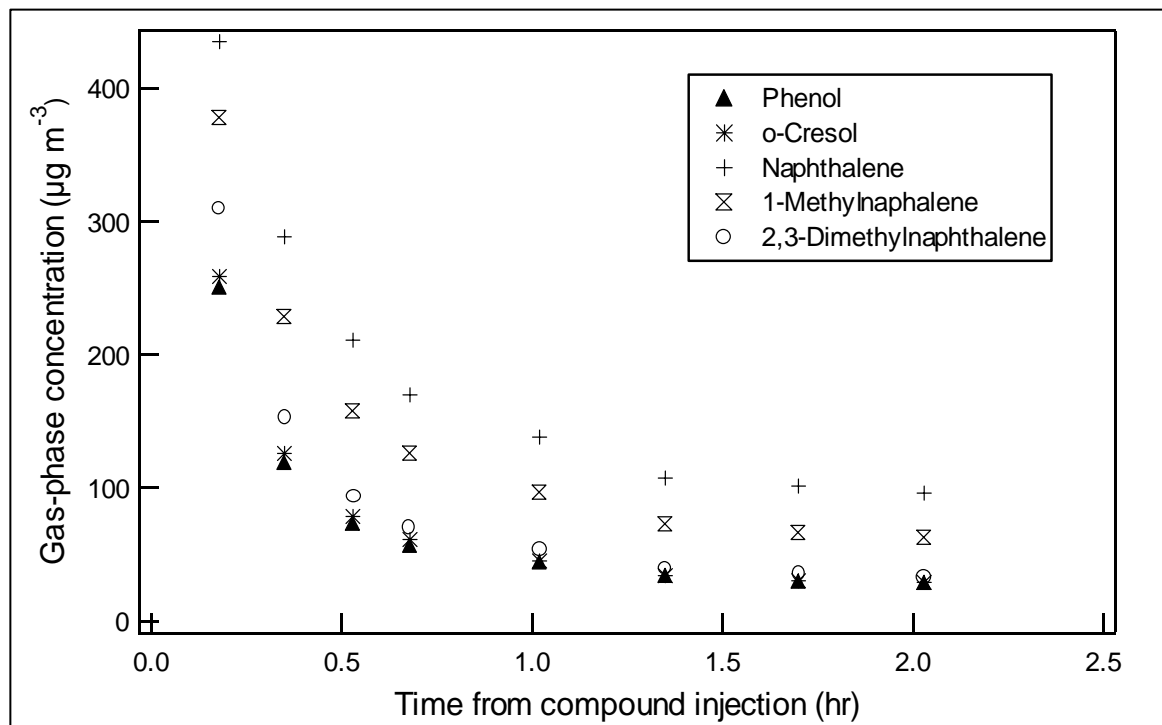
The rise in concentrations of selected compounds, following flushing and resealing, is shown in Figure 8. The increase appears to be linear for about the first two hours for all compounds. By this point, the less volatile, more readily sorbing compounds (e.g. cresol, naphthalene, and methylnaphthalene) have reached the gas-phase concentrations that were present before flushing, indicating a return to equilibrium with the very large reservoir of sorbed mass. The sorbed or surface concentrations of these compounds are essentially unchanged by the flushing and desorption processes. Concentrations of the more volatile compounds continue to increase after the second hour. The declining rate of increase is consistent with an increase of adsorption that accompanies the approach to equilibrium. The sorbed concentrations of these compounds are affected by desorption of a significant amount of mass back to the gas-phase. Future experiments will investigate whether the post-flushing equilibrium relationship is similar to the partitioning that existed at the end of the net adsorption phase.

Another key lesson learned from these pilot experiments pertains to the quantitation of desorption for semi-volatile compounds. The observed rise in concentrations of the SVOC was relatively small compared to the initial concentration after resealing. Increasing the flush time will help reduce the initial concentration upon resealing. We also will add a steady ventilation period at the end of each experiment to measure desorption of SVOC. With ventilation turned on, desorption, adsorption, and removal by ventilation will lead to a dynamic balance that can be used to calculate the desorption rate.

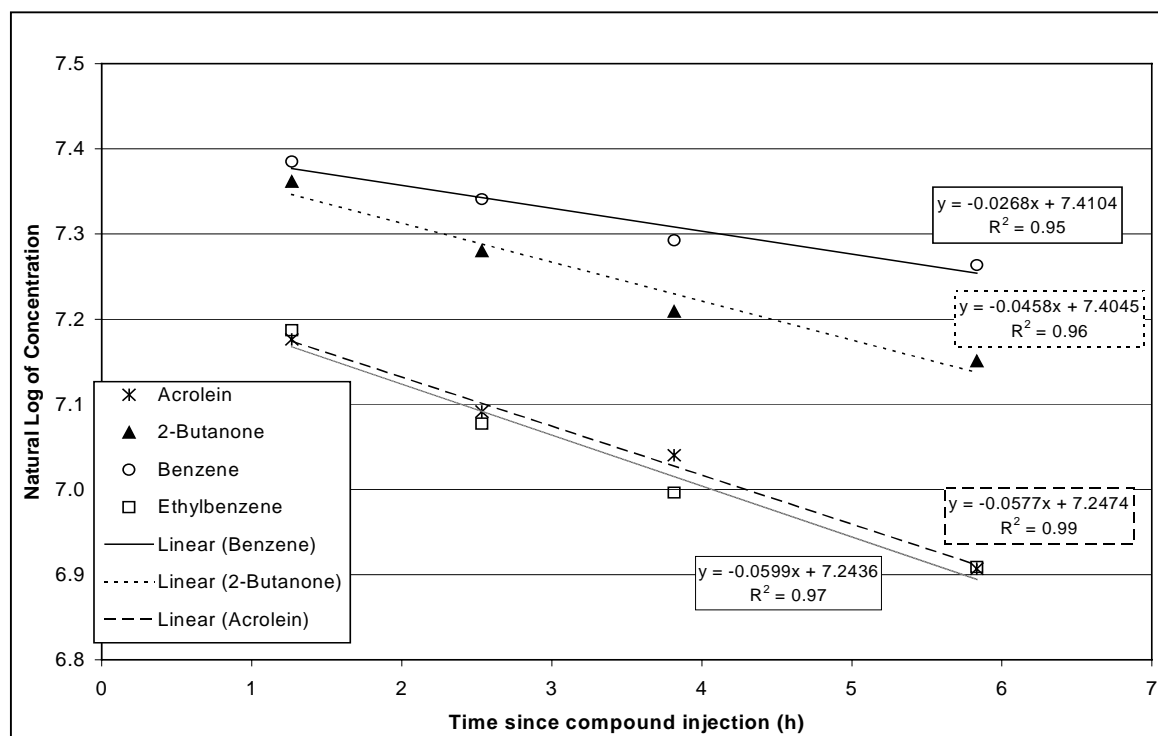
Our research plan calls for one additional experiment while the chamber is still outfitted with the chemically aged surface materials, which have been exposed to a variety of gas-phase organics during several years of experimentation. Following this, the chamber will be retrofitted with new carpet and gypsum wallboard and the other materials will be “cleaned”, e.g. by exposure to VOC-free air at elevated temperatures for the chairs, or by laundering in hot, soapy water for the draperies. We will conduct a series of experiments, most generally as described, but at three distinct temperature levels that span the range encountered in actual residences. Sorption theory suggests that temperature could have a substantial effect on gas vs. sorbed phase equilibrium. The temperature dependence of sorption processes has not yet been carefully measured in a systematic way.



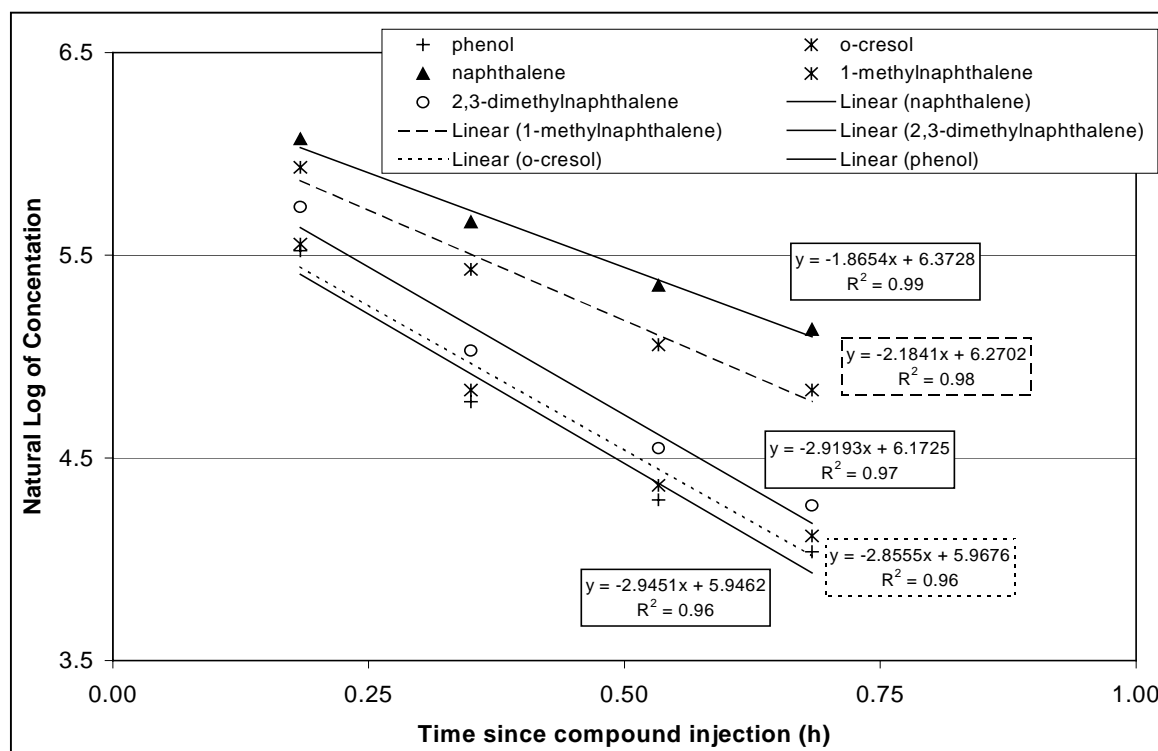
**Figure 6a.** Sorption-induced decay of volatile organic HAPs in a sealed and furnished, 50-m<sup>3</sup> room; from Experiment 1. For these volatile compounds, sorption reduces concentrations over just a few hours approaching equilibrium within about 1 day.



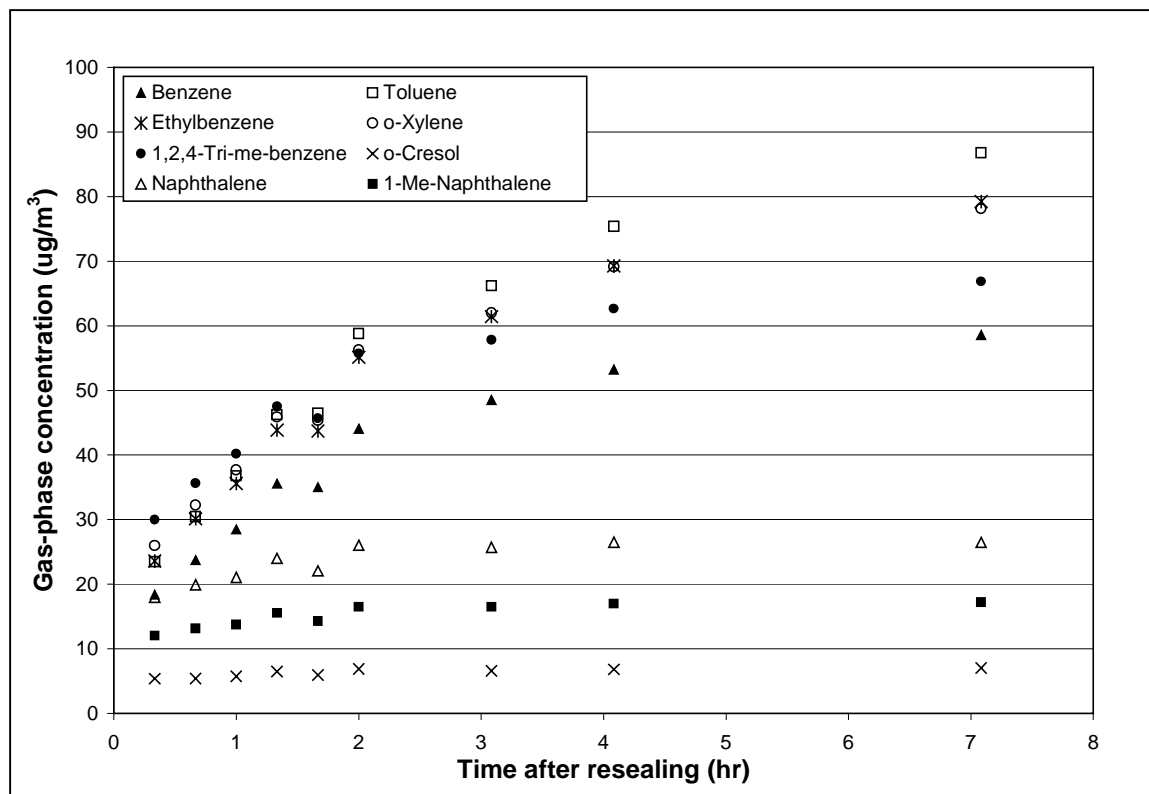
**Figure 6b.** Sorption-induced decay of semi-volatile organic HAPs in a sealed and furnished, 50-m<sup>3</sup> room; from Experiment 3. For these less volatile compounds, sorption reduces concentrations dramatically within tens of minutes, and equilibrium is approached within about 1 hour.



**Figure 7a.** Fitting of measured concentration data to first order decay model to estimate adsorption rate for volatile organic HAPs. First-order coefficients of equations are the adsorption rates, in units of (1/h).



**Figure 7b.** Fitting of measured concentration data to first order decay model to estimate adsorption rate for semi-volatile organic HAPs. First-order coefficients of equations are the adsorption rates, in units of (1/h).



**Figure 8.** Net desorption phase, following flushing and resealing of chamber in experiment 3. The rise in concentrations results from the net desorption of mass sorbed during the net adsorption phase.

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## LITERATURE CITED:

- Borazzo JE, CI Davidson and JB Andelman (1990). Sorption of organic vapors to indoor surfaces of synthetic and natural fibrous materials. Indoor Air '90, Toronto, Canada.
- Carter W. 2000. *Documentation of the saprc-99 chemical mechanism for voc reactivity assessment.*, California Air Resources Board. Contracts 93-329 and 95-308.
- Colombo A, M DeBortoli, H Knoppel, *et al.* 1993. "Adsorption of selected volatile organic compounds on a carpet, a wall coating, and a gypsum board in a test chamber." *Indoor Air* Vol. 3: pp. 276-282.
- Jorgensen RB and O Bjorseth. 1999. "Sorption behaviour of volatile organic compounds on material surfaces - the influence of combinations of compounds and materials compared to sorption of single compounds on single materials." *Environnment International* Vol. 25(No. 1): pp. 17-27.
- Jorgensen RB, O Bjorseth and B Malvik. 1999. "Chamber testing of adsorption of volatile organic compounds (vocs) on material surfaces." *Indoor Air* Vol. 9: pp. 2-9.
- Lee K, J Vallarino, T Dumyahn, *et al.* 1999. "Ozone decay rates in residences." *Journal of the Air & Waste Management Association* Vol. 49(10): pp. 1238-1244.
- Marr LC. 2002. *Changes in ozone sensitivity to precursor emissions on diurnal, weekly, and decadal time scales*. Civil and Environmental Engineering. Berkeley, University of California, Berkeley: 213.
- Nazaroff WW and GR Case. 1986. "Mathematical modeling of chemically reactive pollutants in indoor air." *Environmental Science Technology* Vol. 20(No. 9): pp. 924-934.
- Piade JJ, S D'Andres and EB Sanders. 1999. "Sorption phenomena of nicotine and ethenylpyridine vapors on different materials in a test chamber." *Environmental Science & Technology* Vol. 33(No. 12): pp. 2046-2052.
- Rubin M. Personal communication, August 27.
- Sarwar G, R Corsi, Y Kimura, *et al.* 2002. "Hydroxyl radicals in indoor environments." *Atmospheric Environment* Vol. 36: pp. 3973-3988.
- Van Der Wal JF, AW Hoozeveen and L van Leeuwen. 1998. "A quick screening method for sorption effects of volatile organic compounds on indoor materials." *Indoor Air* Vol. 8: pp. 103-112.
- Van Loy MD, VC Lee, LA Gundel, *et al.* 1997. "Dynamic behavior of semivolatile organic compounds in indoor air. 1. Nicotine in a stainless steel chamber." *Environmental Science & Technology* Vol. 31(No. 9): pp. 2554-2561.
- Van Loy MD, WJ Riley, JM Daisey, *et al.* 2001. "Dynamic behavior of semivolatile organic compounds in indoor air. 2. Nicotine and phenanthrene with carpet and wallboard." *Environmental Science & Technology* Vol. 35(No. 3): pp. 560-567.
- Vuilleumier L, NJ Brown, RA Harley, *et al.* 2000. *Review and improvement of methods for estimating rates of photolysis in photochemical models*, Prepared for the California Air Resources Board. Draft Final Report, Contract No. 96-335.
- Vuilleumier L, JT Bamer, RA Harley, *et al.* 2001. "Evaluation of nitrogen dioxide photolysis rates in an urban area using data from the 1997 Southern California ozone study." *Atmospheric Environment* Vol. 35: pp. 6525-6537.
- Weschler CJ and HC Shields. 1996. "Production of the hydroxyl radical in indoor air." *Environmental Science & Technology* Vol. 30(No. 11): pp. 3250-3258.

- Won D, RL Corsi and M Rynes. 2000. "New indoor carpet as an adsorptive reservoir for volatile organic compounds." *Environmental Science & Technology* Vol. 34(No. 19): pp. 4193-4198.
- Won D, RL Corsi and M Rynes. 2001. "Sorpative interations between vocs and indoor materials." *Indoor Air-International Journal of Indoor Air Quality and Climate* Vol. 11(4): pp. 246-256.
- Won D, DM Sander, CY Shaw, *et al.* 2001. "Validation of the surface sink model for sorptive interactions between VOCs and indoor materials." *Atmospheric Environment* Vol. 35: pp. 4479-4488.

**Appendix Table A-1.** Description of SAPRC-99 individual and lumped species used for the indoor modeling system.

<b>Constant species</b>	
O2	Oxygen
M	Air
H2O	Water
hv	Light
<b>Active Inorganic Species.</b>	
O3	Ozone
NO	Nitric Oxide
NO2	Nitrogen Dioxide
NO3	Nitrate Radical
N2O5	Nitrogen Pentoxide
HONO	Nitrous Acid
HNO3	Nitric Acid
HNO4	Peroxynitric Acid
HO2H	Hydrogen Peroxide
CO	Carbon Monoxide
SO2	Sulfur Dioxide
<b>Active Radical Species and Operators.</b>	
HO.	Hydroxyl Radicals
HO2.	Hydroperoxide Radicals
C-O2.	Methyl Peroxy Radicals
RO2-R.	Peroxy Radical Operator representing NO to NO2 conversion with HO2 formation.
R2O2.	Peroxy Radical Operator representing NO to NO2 conversion without HO2 formation.
RO2-N.	Peroxy Radical Operator representing NO consumption with organic nitrate formation.
CCO-O2.	Acetyl Peroxy Radicals
RCO-O2.	Peroxy Propionyl and higher peroxy acyl Radicals
BZCO-O2.	Peroxyacyl radical formed from Aromatic Aldehydes
MA-RCO3.	Peroxyacyl radicals formed from methacrolein and other acroleins.
<b>Steady State Radical Species</b>	
O3P	Ground State Oxygen Atoms
O*1D2	Excited Oxygen Atoms
TBU-O.	t-Butoxy Radicals
BZ-O.	Phenoxy Radicals
BZ(NO2)-O.	Nitro-substituted Phenoxy Radical
HOCOO.	Radical formed when Formaldehyde reacts with HO2
<b>PAN and PAN Analogues</b>	
PAN	Peroxy Acetyl Nitrate
PAN2	PPN and other higher alkyl PAN analogues
PBZN	PAN analogues formed from Aromatic Aldehydes
MA-PAN	PAN analogue formed from Methacrolein
<b>Explicit and Lumped Molecule Reactive Organic Product Species</b>	
HCHO	Formaldehyde
CCHO	Acetaldehyde
RCHO	Lumped C3+ Aldehydes

ACET	Acetone
MEK	Ketones and other non-aldehyde oxygenated products which react with OH radicals slower than $5 \times 10^{-12}$ cm <sup>3</sup> molec <sup>-2</sup> s <sup>-1</sup>
MEOH	Methanol
COOH	Methyl Hydroperoxide
ROOH	Lumped higher organic hydroperoxides
GLY	Glyoxal
MGLY	Methyl Glyoxal
BACL	Biacetyl
PHEN	Phenol
CRES	Cresols
NPHE	Nitrophenols
BALD	Aromatic aldehydes (e.g., benzaldehyde)
METHACRO	Methacrolein
MVK	Methyl Vinyl Ketone
ISO-PROD	Lumped isoprene product species
<b>Lumped Parameter Products</b>	
PROD2	Ketones and other non-aldehyde oxygenated products which react with OH radicals faster than $5 \times 10^{-12}$ cm <sup>3</sup> molec <sup>-2</sup> s <sup>-1</sup>
RNO3	Lumped Organic Nitrates
<b>Uncharacterized Reactive Aromatic Ring Fragmentation Products</b>	
DCB1	Reactive Aromatic Fragmentation Products that do not undergo significant photodecomposition to radicals
DCB2	Reactive Aromatic Fragmentation Products which photolyze with alpha-dicarbonyl-like action spectrum
DCB3	Reactive Aromatic Fragmentation Products which photolyze with acrolein action spectrum
<b>Non-Reacting Species</b>	
CO2	Carbon Dioxide
XC	Lost Carbon
XN	Lost Nitrogen
SULF	Sulfates (SO <sub>3</sub> or H <sub>2</sub> SO <sub>4</sub> )
INERT	Inert products
<b>Low Reactivity Compounds or Unknown Products Represented as Unreactive</b>	
H2	Hydrogen
HCOOH	Formic Acid
CCO-OH	Acetic Acid
RCO-OH	Higher organic acids
CCO-OOH	Peroxy Acetic Acid
RCO-OOH	Higher organic peroxy acids
<b>Primary Organics Represented explicitly</b>	
CH4	Methane
ETHENE	Ethene
ISOPRENE	Isoprene
<b>Lumped Parameter Species</b>	
ALK1	Alkanes and other non-aromatic compounds that react only with OH, and have $k_{OH} < 5 \times 10^2$ ppm <sup>-1</sup> min <sup>-1</sup> (other than ethane)
ALK2	Alkanes and other non-aromatic compounds that react only with OH, and have $k_{OH}$ between $5 \times 10^2$ and $2.5 \times 10^3$ ppm <sup>-1</sup> min <sup>-1</sup> (other than propane and acetylene)



ALK3	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between $2.5 \times 10^3$ and $5 \times 10^3$ ppm <sup>-1</sup> min <sup>-1</sup>
ALK4	Alkanes and other non-aromatic compounds that react only with OH, and have kOH between $5 \times 10^3$ and $1 \times 10^4$ ppm <sup>-1</sup> min <sup>-1</sup>
ALK5	Alkanes and other non-aromatic compounds that react only with OH, and have kOH > $1 \times 10^4$ ppm <sup>-1</sup> min <sup>-1</sup>
ARO1	Aromatics with kOH < $2 \times 10^4$ ppm <sup>-1</sup> min <sup>-1</sup>
ARO2	Aromatics with kOH > $2 \times 10^4$ ppm <sup>-1</sup> min <sup>-1</sup>
OLE1	Alkenes with kOH < $7 \times 10^4$ ppm <sup>-1</sup> min <sup>-1</sup> (other than ethene)
OLE2	Alkenes with kOH > $7 \times 10^4$ ppm <sup>-1</sup> min <sup>-1</sup> (other than isoprene)
TRP1	Terpenes
<b>Explicitly-represented species of local interest</b>	
MBUTENOL	2-methyl-2-butene-3-ol
ETHANE	Ethane
ACETYLEN	Acetylene
PROPANE	Propane
BENZENE	Benzene
BUTDE	1,3-butadiene
MTBE	Methyl t-butyl ether
ETOH	Ethanol

Appendix Table A-2. Deposition velocities from Nazaroff and Cass (1988) used in alpha model.

Compound(s)	Deposition velocity (cm s <sup>-1</sup> )
Ozone (O <sub>3</sub> )	0.036
NO <sub>2</sub>	0.006
HCHO, RCHO	0.005
PAN	0.035
HNO <sub>2</sub> , HNO <sub>3</sub> , HNO <sub>4</sub> , HO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> , NO <sub>3</sub> , N <sub>2</sub> O <sub>5</sub> , RCO <sub>3</sub> , RNO <sub>4</sub> , RONO, RO <sub>2</sub>	0.07